






## METHOD FOR THE PRODUCTION OF FATTY ACID ESTERS OF LOWER ALCOHOLS

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**Abstract of WO 0238529 (A1)**

The invention relates to a method for the production of fatty acid esters of lower alcohols, in particular of methanol, from the glycerine phase accumulated during the base-catalysed transesterification of fatty acid glycerides, in particular with methanol. The fatty acids formed from the neutralisation of the glycerine phase are esterified with lower alcohols, preferably with methanol and concentrated sulphuric acid. The phase, comprising sulphuric acid, methanol and water, obtained after the phase separation of the esterification mixture is used for neutralisation of the glycerine phase.

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Method to the preparation of fatty acid esters of low alcohols the instant invention concerns a method to the preparation of fatty acid esters of low alcohols with 1-4 C-atoms, in particular the methanol, by neutralization of the alcohols, in particular the methanol, low with the alkali-catalyzed transesterification of Fettsäureglyceriden with low alcohols, in particular with methanol, as byproduct of resulting heavy phase, the so called Glycerinphase, and by sulfuric acid-catalyzed esterification of the mixture of free fatty acids and fatty acid esters, obtained suitable to the use as Diesel replacement materials (bio Diesels), with the neutralization of the Glycerinphase, with low alcohols with 1-4 C-atoms, preferably with methanol.

Fatty acid esters of low alcohols in particular the methanol have lately major importance as Diesel replacement materials (bio Diesel) obtained. Such methods become for example in the RK 397,510 B and the EP 708,813 A described. These and most other methods use alkali metal hydroxide or alcoholates than catalysts for the transesterification of Fettsäureglyceriden such as z. B. Rapeseed oil, sunflower oil or used Speisefetten with low alcohols, in particular with methanol, whereby a byproduct referred as Glycerinphase results, which contains a substantial portion at alkali salts of fatty acids and at fatty acid esters of the alcohol used to the transesterification beside glycerol. The Glycerinphase is worthless in this form economic and represents a disposal product. The fatty acids and fatty acid ester contained in it worsen the yield to bio Diesels and thus the economy of a bio Diesel plant.

It is known that in the Glycerinphase the fatty acids contained as alkali salts and the fatty acid esters by neutralization with an acidic one isolated to become to be able. Such a method becomes in the RK 392,977 B described.

The obtained mixture from free fatty acids and fatty acid esters is however more usable due to the high content at free fatty acids not as diesel fuel and possesses likewise no economic value.

From the text books of the organic-preparative chemistry, for example "Organikum" 13. Aufl. 1974, S 441ff or Weygand/Hilgetag, "organic Chemical experimentation art, 4. Aufl. 1970, S 377ff, are known that Carbonsäure-bzw. Fatty acid ester by esterification of the free acids with low alcohols preferably with boiling temperature of the alcohols in Presence of strong acidic ones, like hydrogen chloride, sulfuric acid or Sulphonic acids esterified to become to be able.

A method to the esterification from the Glycerinphase isolated Fatty acid/fatty acid ester mixture becomes described in the EP 708,813 A, whereby the free obtained from the neutralization of the Glycerinphase Fatty acids with methanol and concentrated sulfuric acid as catalyst two Hours on 85 C heated become, whereby that content at free fatty acids of approx. 50% to 12,5% decrease/go back and the whole mixture without other Treatment of a alkali-catalyzed transesterification supplied becomes and those Catalyst-acidic over the transesterification process is removed.

Other methods to the esterification from free fatty acids become into that EP 127104 A and EP 184,740 A described, whereby the free fatty acids in a mixture with Fettsäuretriglyceriden are present and the esterification through Heating with methanol with 65 C with sulfuric acid or a sulphonic acid as Catalyst conducted becomes.

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As esterification catalysts mostly concentrated sulfuric acid becomes, Benzene, p-toluene, or methanesulfonic acid used. A problem with that Application of this acidic ones places the utilization and/or. Disposal that Catalyst-acidic. The acidic ones must either regenerated, i.e. dewatered will to be able or it become to become over as catalysts again used for example a alkali-catalyzed transesterification process supplied or neutralized and to arrive as biological not degradable salts into the effluent or to fall as worthless byproducts on.

The object of the instant invention consists of it, an improved process to the recovery of fatty acid esters of low alcohols, preferably the methanol suitable as Diesel replacement materials, making available from the Glycerinphase resulting with the alkali-catalyzed transesterification of Fettsäureglyceriden with low alcohols which avoid the disadvantages mentioned and a fatty acid ester suitable as diesel fuel supplies and one recovers further into the Glycerinphase contained low alcohols and one receives a Rohglycerin with 60 to 90% Glycerinanteil.

The invention process is characterised in that one A) the esterification of the mixture from free fatty acids and fatty acid esters of low alcohols, in particular the methanol, with an excess of a low alcohol with 1-4 C-atoms, preferably

methanol, in presence of concentrated sulfuric acid, obtained from the neutralization of the Glycerinphase, accomplishes, whereby the reaction mixture preferably separates according to made esterification into a phase existing from the fatty acid ester of the low alcohol, preferably the methanol, and into a phase existing from the excess low alcohol methanol, sulfuric acid and reaction water, and that manb) those the fatty acid esters of the low alcohols contained phase into actual known way by treating with alkali hydroxides, preferably caustic potash solution, by washing also Water and/or acidic one and evaporation of the excess low alcohol clean, and that one C) the phase existing from the excess low alcohol preferably methanol, sulfuric acid and reaction water to the neutralization of an other Glycerinphase used, whereby itself the neutralized mixture into a light phase existing from free fatty acids, fatty acid esters of low alcohols preferably the methanol and free low alcohols preferably methanol and into a heavier phase existing from glycerol, which excess low alcohol, preferably methanol, and alkali sulfate separate.

In accordance with an other feature of the invention the esterification of the mixture obtained from the neutralization of the Glycerinphase does not become from free fatty acids and fatty acid esters of low alcohols conducted with temperatures over 50 C, preferably not over 40 C and particularly preferably not over 35 C. Thus an optimum manufacture process, which favourable-proves is still energy-saving, becomes ensured.

After an other embodiment of the invention the concentrated sulfuric acid in a concentration of 0,5-17 Masse%, serving as catalyst, becomes related to the mass fatty acid of the fatty acid ester mixture used. The used amount sulfuric acid is at the most equally large thereby or more minor as to the neutralization in the Glycerinphase contained amount at alkali soaps of requisite amount. If the amount used to the esterification is more minor sulfuric acid, than to the neutralization of the Glycerinphase necessary would be, neutralized becomes with additional sulfuric acid.

In accordance with an other feature of the invention become the low alcohols with 1-4 C-atoms in an amount from 15 to 200 Masse% used related to the amount of the fatty acid/fatty acid ester mixture. In addition as low alcohols with 1-4 C-atoms come ethanol, 1-und 2-Propanol, 1-Butanol, 2-Butanol and isobutanol into question.

After an other embodiment of the invention the esterification of the fatty acid/fatty acid ester mixture along that becomes low alcohols and the concentrated sulfuric acid bottom intensive agitation with generation as major a turbulences in a period of 0,5 to 3 hours conducted as possible. The esterification reaction becomes thus accelerated by intensive agitation bottom formation as major a turbulences as possible, whereby the degree of esterification is after 0,5 to 3 hours more than 95 percent.

In accordance with a development of the invention methanol becomes used as low alcohol. After an other embodiment of the invention will the phase existing from the fatty acid esters of the low alcohols, preferably the methanol, which contains still minor proportions at free fatty acids, into actual known way with alkali hydroxides, preferably caustic potash solution, treated and by water washing and/or diluted acidic one and evaporation of the excess low alcohol purified or can into the wash process of a bio Diesel plant be transferred.

As Glycerinphasen preferably become such used, which become obtained with potassium hydroxide or the potassium-alcoholate-catalyzed transesterification of Fettsäureglyceriden with low alcohols.

Distillative knows the heavy phase existing from glycerol, excess low alcohol and alkali sulfate, resulting with the neutralization of the Glycerinphase, to low alcohol, into the esterification recycled and a Rohglycerin with 60-90 per cent the Glycerinanteil and in solid alkali sulfate, which in case of of potassium sulfate as fertilisers in the agriculture use can find, will be regenerated.

A particular advantage of the invention process is to be seen in the fact that the sulfuric acid both when catalyst to the esterification and subsequent to the neutralization of the Glycerinphase used will, so that becomes required for both processes only a single adjuvant, that into an alkali sulfate, preferably potassium sulfate, converted, that as fertiliser in the agriculture application will find can and that no biological not degradable products such as sulphonic acids and/or. their salts as waste products result, and that the esterification energy-saving with moderate temperatures with high degrees of esterification of over 95% made. The method comes to meet thereby beside the economic also the ecological requirements of the bio Diesel production.

An other advantage of the invention process consists of the fact that to the neutralization of the alkali salts of the fatty acids into the Glycerinphase requisite amount sulfuric acid exceeds to the esterification the the same amount fatty acid requisite amount by far, so that the esterification relative high sulfuric acid concentrations used to become to be able, which with the low temperatures and times of 0,5-3 hours cause an high degree of esterification.

An other advantage is to be seen in the fact that into the Glycerinphase contained low alcohols derived from the transesterification are recovered, and a Rohglycerin with a Glycerinanteil from 60 to 90% recovered becomes.

The invention becomes near explained by the subsequent examples: Example 1) 100 grams of a mixture existing from 65% RWS fatty acids, 26% RWS methyl ester and 9% methanol become with 70 grams methanol and 11.3 grams concentrated sulfuric acid 2 hours with a temperature of 30 C with a wing agitator intensive agitated. According to turning the stirrer off the mixture separates into 108 grams of an ester phase existing from 99.3 grams RWS methyl ester, 0.7 grams RWS fatty acids and 8 grams methanol and 73.3 grams of a phase existing from 11.0 grams sulfuric acid, 58.3 grams methanol and 4 grams reaction water.

The ester phase (108 grams) becomes the other purification with 0.35 grams 50 of a per cent caustic potash solution offset and 2 minutes agitated. The mixture separates according to turning the stirrer off errs 5 grams heavier phase existing from the potassium salts of RWS fatty acids, methanol and water and in 103 grams easier ester phase.

The ester phase becomes now first remote with water and subsequent with diluted sulfuric acid washed and the excess methanol in a rotary evaporator.

The so obtained RWS fatty acid methyl ester contains less as 0.2% free fatty acids and met all remaining requirements to the utility than diesel fuel.

The phase (73.3 grams) existing from 11.0 grams sulfuric acid, 58.3 grams methanol and 4 grams reaction water is let flow separated and bottom agitations to 300 grams of a Glycerinphase, which originates from a transesterification catalyzed with potassium hydroxide from rapeseed oils with methanol and the subsequent composition has:

73 grams of potassium salts of RWS fatty acids

26 grams RWS methyl ester 100 grams glycerol

56 grams methanol

45 grams of water the neutralized mixture to the separation by solid potassium sulfate filtered is centrifuged or, according to which itself the filtrate in 100 grams of an easier phase existing from 65 grams RWS fatty acids, 26 grams RWS methyl esters and 9 grams methanol and 246 grams of a heavier phase, which glycerol, methanol and water contain, and after evaporation of the methanol a Rohglycerin. with at least 60% Glycerinanteil results in.

Example 2) 100 grams of a mixture existing from 40% fatty acids, 52% fatty acid more hylester and 8% methanol become with 120 grams methanol and 2,8 grams concentrated sulfuric acid 2 hours with a temperature of 50 C with a magnetic stirrer intensive agitated. According to turning the stirrer off the reaction mixture separates into 102 grams of an ester phase existing from 93.6 grams fatty acid methyl ester, 0.4 grams free fatty acids and 8 grams methanol, and into 120.8 grams of a phase existing from 2.7 grams sulfuric acid, 2.5 grams reaction water and 115 grams methanol.

The ester phase (102 grams) becomes the weitren purification with 0.30 grams of a 30-prozentigen solution of potassium hydroxide in methanol offset, 2 minutes agitated, and as in example 1) other-proceed. The so obtained fatty acid methyl ester contains 0.08% free fatty acids.

The phase (120.8 grams) existing from 2.7 grams sulfuric acid, 2.5 grams of water and 115 grams methanol is let flow separated and bottom agitations to 323 grams of a Glycerinphase, which originates from a transesterification of an used Fritieröles with methanol, catalyzed with potassium hydroxide, and the subsequent composition has: 46 grams of potassium salts of fatty acids 52 grams fatty acid methyl ester 100 grams glycerol 65 grams methanol of 60 grams of water to other neutralization become still 9.6 grams 50-prozentige sulfuric acid added.

The neutralisierte mixture is centrifuged to the separation by solid Kaluimsulfat filtered or, according to which itself the filtrate in 100 grams of an easier phase existing from 40 grams fatty acids, 52 grams fatty acid methyl esters and 8 grams methanol and 350 grams of an heavy phase, which glycerol contains methanol and water.

The easier phase becomes an other esterification as initially described, supplied in this example.



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Claims 1. Method to the preparation of fatty acid esters of low alcohols with 1-4 C, suitable to the use as Diesel replacement materials (bio Diesels)

Atoms, in particular the methanol, by neutralization with the alkali-catalyzed transesterification of Fettsäureglyceriden with low

Alcohols, in particular with methanol, as byproduct of resulting heavy phase, the so called Glycerinphase and by sulfuric acid-catalyzed esterification with the neutralization that

Glycerinphase of obtained mixture of free fatty acids and

Fatty acid esters of low alcohols, in particular the methanol, with low alcohols with 1-4 C-atoms, preferably with methanol, characterised in that one A) the esterification of the mixture from free fatty acids and fatty acid esters of low, obtained from the neutralization of the Glycerinphase

In particular the methanol with an excess of a low alcohol with 1-4 C-atoms methanol in presence of concentrated sulfuric acid preferably accomplishes alcohols, whereby itself that

Reaction mixture after made esterification into a phase existing from the fatty acid ester of the low alcohol, preferably the methanol and into a phase existing from the excess low alcohol, preferably methanol, sulfuric acid and reaction water separates, and that one b) those the fatty acid esters of the low alcohols contained phase in actual known way by treating with alkali hydroxides, preferably

Caustic potash solution, by water washing and/or acidic one and evaporation of the excess low alcohol cleans, and that one C) the phase existing from the excess low alcohol preferably methanol, sulfuric acid and reaction water to Neutralization of an other Glycerinphase used, whereby itself the neutralized mixture into a light phase existing from free

Fatty acids, fatty acid esters of low alcohols in particular the methanol and free low alcohols preferably methanol and into a heavier

Phase existing from glycerol, which excess low alcohol, preferably methanol, and alkali sulfate separate.

2. Process according to claim 1, characterised in that the esterification of the mixture from free fatty acids and fatty acid esters of low alcohols with temperatures over 50 C, preferably not over 40 C and particularly preferably not over 35 C conducted, obtained from the neutralization of the Glycerinphase, does not become.

3. Process according to claim 1 or 2, characterised in that as

Catalyst serving concentrated sulfuric acid in an amount from 0,5 to 17 Masse% related to the mass fatty acid Fatty acid ester mixture used becomes.

4. Method after at least one of the claims 1 to 3, characterised in that the low alcohols with 1-4 C-atoms in one Amount from 15 to 200 percent related to the amount fatty acid Fatty acid ester mixture used become.

5. Method after at least one of the claims 1 to 4, characterised in that the esterification fatty acid

Fatty acid ester mixture with the low alcohols and the concentrated

Sulfuric acid bottom intensive agitation with generation as more major as possible

Turbulences in a period of 0,5 to 3 hours conducted becomes.

6. Method after at least one of the claims 1 to 5, characterised in that as low alcohol methanol used becomes.

7. Method after at least one of the claims 1 to 6, characterised in that one the fatty acid esters of the low alcohols, preferably the methanol, after which treatment with alkali hydroxides, preferably, into the wash process of a bio Diesel plant transfers caustic potash solution.

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